

# COATINGS

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## STRUCTURE AND PROPERTIES OF NANOPRODUCTS OF THE SYSTEM $P_2O_5 - SiO_2$

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Thin films and dispersed products in the system  $SiO_2 - P_2O_5$  with phosphorus oxide molar content from 0 to 30% have been obtained by the sol-gel method from film-forming solutions based on tetraethoxysilane and phosphoric acid, ethyl alcohol, and water. The variations of the rheological properties in successive states of the solution – sol-gel system are established. The physical – chemical processes in solution with deposition on a substrate and with heat-treatment of the product are investigated. IR spectroscopy and atomic-force microscopy are used to study the structure and physical – chemical properties of the films and disperse products obtained.

The sol-gel technology is being increasingly used to obtain oxide ceramic, glass ceramic, and glassy materials. This method for synthesizing materials in oxide systems makes it possible to extend the boundaries of the glass-formation zone and, correspondingly, the composition range for practical applications [1, 2]. Silicophosphate glasses, both binary and polycomponent, conventionally are used to obtain optical media, and in recent decades in other areas also [3 – 5]. The production of silicophosphate glasses by the conventional melting of the initial materials together is a laborious process that is difficult to control, which results in uncertain composition and instability of the properties of the glass produced. At the same time, it is precisely the sol-gel methods of synthesis, specifically, of bioglass, together with the technological advantages that has a positive effect on the bioactive properties of the materials obtained [6].

The purpose of the present work was to obtain materials in the system  $SiO_2 - P_2O_5$  with phosphorus oxide content from 0 to 30%<sup>2</sup> by the sol-gel method and to investigate their structure and physical – chemical properties.

The materials were obtained in a finely dispersed powder state and in the form of films from film-forming solutions (FFS). They were prepared on the basis of 96% analytically pure (AP) ethyl alcohol, AP tetraethoxysilane (TEOS), and AP orthophosphoric acid with solution concentration

0.4 moles/liter. The films were obtained on different amorphous and crystalline substrates by centrifuging with rotational speeds 4000 rpm or drawn at the rate 5 mm/sec followed by heat-treatment at different temperatures. The powder materials were obtained by dryng FFS after they were completely aged.

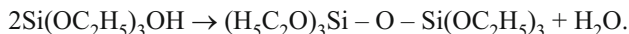
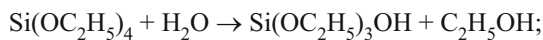
The physical – chemical processes occurring in the solutions and during treatment of the products obtained from them were studied by means of viscosimetry (VPZh-2, temperature 25°C), IR spectroscopy (Perkin Elmer “Spectrum One”), and mass-spectrometric analysis. The thermal analysis of the thin-film systems was performed on a setup using microbalances based on a piezoelectric resonator with weighing accuracy  $10^{-8}$  g. Atomic-force (Solver P47) and electron (Phillips SEM 515 scanning electron microscope) microscopy were used to study the composition and structure of the films. The index of refraction and the thickness of the films were measured with a laser ellipsometer (LEF-3M). The calculations of the optical parameters were performed using a model with a uniform nonabsorbing layer on an isotropic substrate. The electrophysical properties of the films were studied on an E7-8 apparatus. Sclerometry was used to determine the adhesion of the films.

The sol-gel method is based on the capability of the initial substances to enter into a hydrolytic polycondensation reaction and form colloidal solutions, whose viscosity increases during the holding-aging period, on account of which the colloidal solution acquires film-forming properties.

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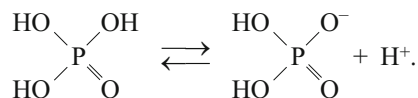
<sup>2</sup> Here and below, unless otherwise stated, the molar content.

For the experimental FFS compositions, films appear after a solution has aged for 2 days. Figure 1 shows the time variation of the viscosity of FFS based on TEOS and phosphoric acid, whose concentration was varied over the range 0–0.224 moles/liter. As one can see, the viscosity of the freshly prepared solution of TEOS in a water-alcohol mixture changes appreciably with time as a result of hydrolysis and polycondensation according to the reactions

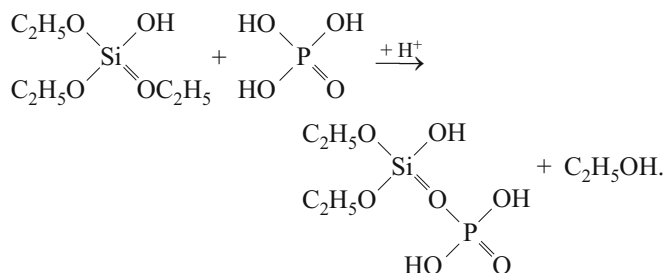


After 2 days the processes slow down and the viscosity changes slowly. The hydrolysis and polycondensation reactions continue but they proceed at a slow rate because of spatial difficulties. After tetra- and pentasiloxanes with terminal OH groups accumulate in the solution, the viscosity starts to increase as a result of ring formation due to the mobility of the Si–O bond [7]. After some time the solution transforms from a sol into a gel. Films made from these solutions are nonuniform, and often they separate, which makes them unsuitable for use.

When  $H_3PO_4$  is introduced into the system, the rheological properties of the FFS stabilize in 1 day. This is explained by acceleration of hydrolysis and polycondensation as a result of an increase of the acidity of the medium. At the same time, the time interval during which FFS are suitable for obtaining films becomes longer (see Fig. 1, curve 2). This is because the spatial obstacles created by the volume anions  $H_2PO_4^-$ ,  $HPO_4^{2-}$ , and less often  $PO_4^{3-}$  impede ring formation of siloxanes. The phosphoric acid is quite strong at the first step of dissociation:

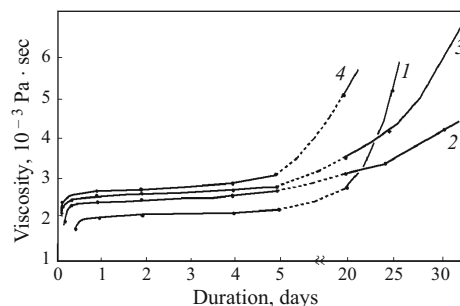


The anion formed substitutes nucleophilically for the ethoxy- or hydroxyl- group of siloxane:



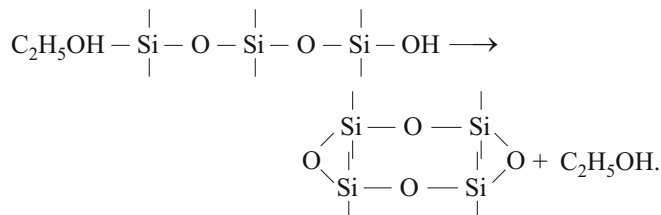
For a high concentration of phosphoric acid, the spatial obstacles are of little consequence as compared with its catalyzing action and, consequently, the viscosity increases sharply at relatively early stages of the FFS aging and gel-formation in the solution (see Fig. 1, curves 3 and 4).

When FFS is deposited on a substrate at 25°C (according to the data from weight analysis) the mass of the film decreases by 25% in 15–20 min. Evidently, the diluent evapo-

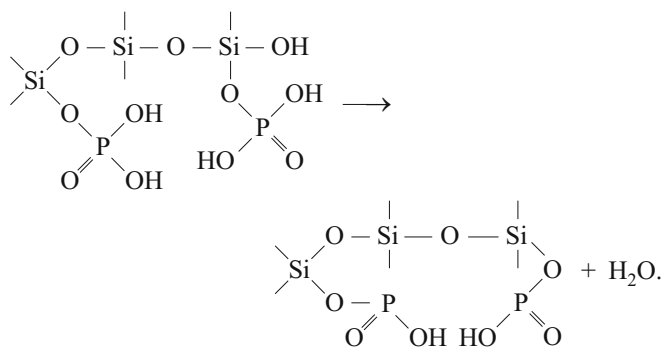


**Fig. 1.** FFP viscosity versus time: 1) no  $H_3PO_4$ ; 2, 3, 4)  $H_3PO_4$  concentration  $5.96 \times 10^{-2}$ ,  $13.4 \times 10^{-2}$ , and  $22.4 \times 10^{-2}$  moles/liter, respectively.

rates from the surface first, and then ring formation of polyorganosiloxanes occurs; this is confirmed by the absence of the vibrational bands of Si–OH groups in the IR spectra (Table 1). In a system with no  $H_3PO_4$  the following process of ring formation of siloxanes occurs:



In the presence of  $H_3PO_4$  the anions  $H_2PO_4^-$  become incorporated into a framework of the cyclic compounds formed:



Additional bands, due to the vibrations of the bonds P–O, P=O, P–OH, P–O–P, and P–O–C, appear in the IR spectra of the films. An increase of the phosphoric acid content in the solution promotes increasingly stronger manifestation of the hydrogen bonds. This is indicated by the displacement of the band due to the vibrations of the P=O bond as well as the appearance of a wide diffuse band in the region  $2703 - 2564 \text{ cm}^{-1}$ , responsible for the vibrations of the OH group of the phosphate ion.

After preliminary hydrolysis (25°C), some unreacted ethoxy- groups remain in the film. When the film is thermostated at 60°C, its mass decreases by 50% in 15–20 min, after which the mass stops changing. The presence of stretching and deformation vibrations of the OH groups is recorded

TABLE 1.

Vibrations (type)	Presence of bands in the IR spectrum, $\text{cm}^{-1}$ , at calcination temperature, $^{\circ}\text{C}$					
	25	60	100	200	500	600
H – O – H	–	3550	3660	3680	–	–
Si – O – H						
Stretching:						
CH <sub>2</sub>	2995	2995	2935	2935	2935	–
CH <sub>3</sub>	2870	2865	–	–	–	–
$\begin{array}{c} \text{H} \\ \diagdown \\ \text{O} \\ \diagup \\ \text{H} \end{array}$	–	1640	1640	1640	1640	–
Deformation:						
CH <sub>2</sub>	1455	1455	–	–	–	–
CH <sub>3</sub>	1400	1400	–	–	–	–
Si – O – Si	1175	1090	1095	1100	1100	1100
	1090	–	–	–	–	–
$\begin{array}{c} \text{H} \\ \diagdown \\ \text{O} - \text{Si} \end{array}$	–	960	–	–	–	–
Si – O – Si	800	800	800	800	800	800
	600	600	600	–	–	–
$\begin{array}{c} \text{O} \\ \diagdown \\ \text{O} - \text{Si} \end{array}$	465	460	460	460	460	460
P – OH	2703	2600	2600	–	–	–
P = O	1250	–	–	–	–	–
Stretching:						
P – O	1190	1190	1190	1190	1190	1190
P – O – C	1050	1050	1050	–	–	–
PO <sub>4</sub> <sup>3–</sup> , HPO <sub>4</sub> <sup>2–</sup> , H <sub>2</sub> PO <sub>4</sub> <sup>–</sup>	1100	–	–	–	–	–
P – O – P	1000	1000	1000	1000	1000	1000

in the IR spectra (see Table 1) of the films at this stage. Gas release with step heat-treatment of FFS (according to mass-spectrometry) is reflected in Table 2. The mass spectra indicate the release of ethyl alcohol and acetic acid. This is explained by the fact that adsorbed water, which initiates the hydrolysis of polysiloxanes present on the surface, is released from the substrate material. In the process alcohol is released:

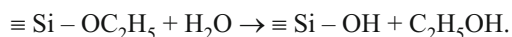
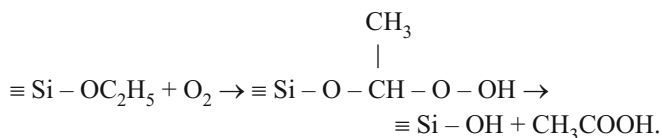


TABLE 2.

Gaseous product	Mass content ( $10^{-5}\%$ ) at treatment temperature ( $^{\circ}\text{C}$ )					
	60	100	200	300	400	500
H <sub>2</sub> O	0	7532	1250	5600	140	0
CO <sub>2</sub>	0	0	0	0	3	52
C <sub>2</sub> H <sub>5</sub> OH	1400	180	58	620	110	0
CH <sub>3</sub> COOH	63	0.8	0	39	14	0.8
C <sub>x</sub> H <sub>y</sub>	0	0	0	0	39	4

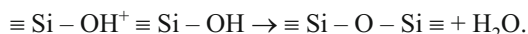
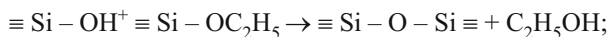
On the other hand, oxidation of the ethoxy-groups by atmospheric oxygen with formation of acetic acid is possible on the surface of the film. This process occurs with formation of radicals by a mechanism which results in the formation of an intermediate product — hydroxoperoxide and as final products — acetic acid and organosiloxanes:



When the film is allowed to stand at  $60^{\circ}\text{C}$  (see Table 1), the hydrolysis, polycondensation, and ring formation of siloxanes on the surface of the film with release of ethanol and acetic acid is completed.

The data from thermal analysis (Fig. 2), IR spectroscopy, and mass spectrometry (see Tables 1 and 2), performed for the condensed products of FFS — films and powders, clearly show two endothermal effects ( $110$  and  $380^{\circ}\text{C}$ ) and one exothermal effect ( $590^{\circ}\text{C}$ ). The endothermal effects are due to the evaporation of water (in the first case) from the surface

and interior volume of the silica particles as a result of the formation of condensed silanol groups with the appearance of siloxane bonds (condensation according to the OH groups) and splitting-off of water and alcohol forming in the process of oxidative thermal destruction (in the second case). The exothermal effect is associated with the combustion of alcohol and products of thermal oxidative destruction of ethoxy groups:



The introduction of phosphoric acid into the initial solution weakens the endothermal effects and shifts them to higher temperatures. At the same time, the temperature of the processes in a series of solutions containing phosphoric acid decreases as the H<sub>3</sub>PO<sub>4</sub> concentration increases.

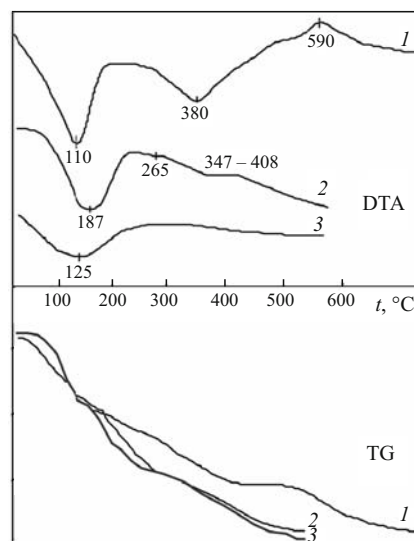
A structure-sensitive parameter — the index of refraction — and the thickness were measured for the films obtained (Table 3). As one can see, the films are relatively thin at the initial stage of ripening of the FFS; the thickness is in the range 73 – 162 nm. Thicker films form as the holding time of the FFS and H<sub>3</sub>PO<sub>4</sub> concentration increase; this is in agreement with the rheological data. The viscosity of the solutions increases as the FFS holding time increases. The films obtained from such solutions have a loose structure and, correspondingly, their refractive indices are lower.

The refractive indices of the materials based on different modifications of SiO<sub>2</sub> and films with the composition SiO<sub>2</sub> are presented below as functions of the calcination temperature.

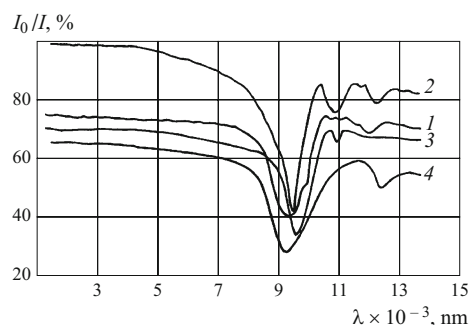
Material	Refractive index
Quartz . . . . .	1.540 – 1.550
Cristobalite . . . . .	1.487 – 1.484
Tridimite . . . . .	1.473 – 1.470
Quartz glass . . . . .	1.458
SiO <sub>2</sub> film for calcination temperatures, °C:	
500 . . . . .	1.440 – 1.450
700 . . . . .	1.459 – 1.463
1000 . . . . .	1.481

The index of refraction of the SiO<sub>2</sub> films treated at 500°C is 1.45, which is characteristic for the amorphous structure of quartz glass. Calcination of the films at 1000°C increases the refractive index to 1.48, which could attest to partial crystallization of the films.

A change of the structure of the films is also observed in the IR-spectroscopy data (Fig. 3). Analysis of the absorption spectra of the films allows drawing a conclusion about the character of the structural order of film oxide. The overall form of the spectrum (position of its main peaks, ratio of the absorption magnitudes) is close to the form of the spectrum of amorphous fused quartz, in whose amorphous structure the initial structural cell is a silicon – oxygen tetrahedron. On the other hand, some fine features of the IR spectrum defi-



**Fig. 2.** DTA and TG curves for FFS (film material) without P<sub>2</sub>O<sub>5</sub> (1) and with P<sub>2</sub>O<sub>5</sub> molar content 5% (2) and 30% (3), respectively.



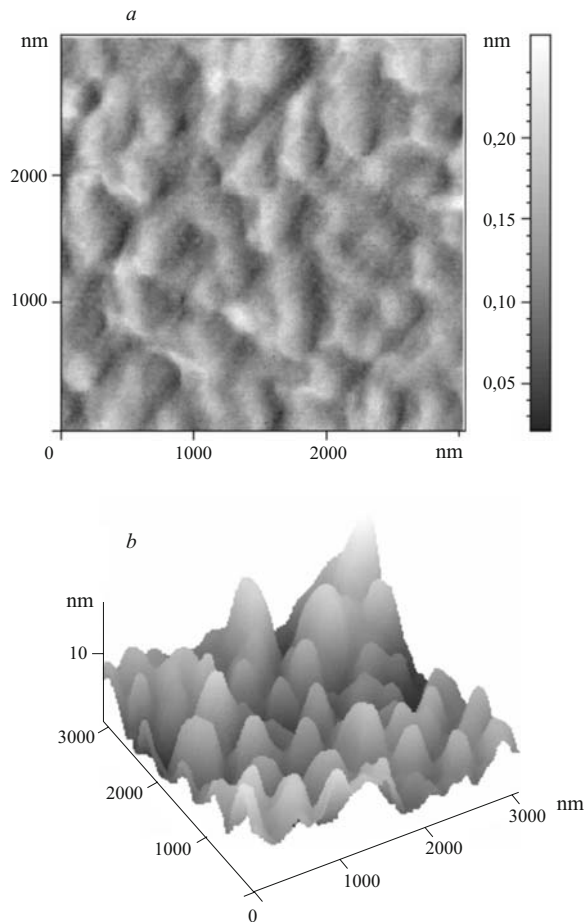
**Fig. 3.** IR absorption spectra of SiO<sub>2</sub> modifications: 1) layered structure; 2) chain structure; 3 and 4) SiO<sub>2</sub> films with calcination temperature 500 and 1000°C, respectively.

nitely indicate the presence of a more developed, as compared with a tetrahedron, order; a definite structural configuration of tetrahedra (chain, layered) dominates, i.e., the structure possesses a definite degree of long-range order.

The spectrum of SiO<sub>2</sub> chain structures contains a wide band in the region (9 – 11.5) × 10<sup>−3</sup> nm. The fact that the po-

**TABLE 3.**

P <sub>2</sub> O <sub>5</sub> molar content, %	Film thickness, nm		Index of refraction of the film	
	4 days	21 days	4 days	21 days
0	—	204	—	1.451
5	162	187	1.481	1.462
10	122	184	1.485	1.468
15	134	197	1.497	1.468
20	141	214	1.495	1.468
25	84	248	1.487	1.453
30	73	—	1.469	—



**Fig. 4.** Results of atomic-force microscopy for  $\text{SiO}_2$  films. Image of the surface relief: a) top view; b) side view.

sition of the computed peaks of the chain structures is identical to that of the two main absorption peaks found experimentally for the films ( $10 \times 10^{-3}$  and  $11.5 \times 10^{-3}$  nm), processed at temperature  $500^\circ\text{C}$ , supports a chain structure of the film obtained. However, the spectrum of the  $\text{SiO}_2$  film processed at  $660^\circ\text{C}$  is characterized by a deep main band in the region  $(9.4 - 10) \times 10^{-3}$  nm and much weaker peaks near  $12 \times 10^{-3}$  nm, which corresponds more closely to the spectrum of a layered structure. In turn, a layered structure can be represented in the form of tetrahedra linked at the vertices via an oxygen atom of the two blocks of a chain structure. The neighboring layers are bound by van der Waals forces and the chemical composition is  $\text{SiO}_2$ .

In summary, it can be supposed that the  $\text{SiO}_2$  films calcined at  $500^\circ\text{C}$  are amorphous with preservation of the order of chain and layered configurations (similar to a block material), but as the calcination temperature increases to  $1000^\circ\text{C}$ , it becomes possible to obtain films with a crystalline structure.

An investigation of structure using an atomic-force microscope was performed for thin films based on  $\text{SiO}_2$ , obtained by the sol-gel method from solutions with viscosity

**TABLE 4.**

$\text{P}_2\text{O}_5$ molar content, %	Refractive index of films with different thickness		Adhesion force, MPa
	$n$	$d$ , nm	
0	—	—	9.8
5	1.481	162	9.6
10	1.485	122	9.5
15	1.497	134	9.2
20	1.495	141	8.8
25	1.487	84	8.6
30	1.469	73	8.1

$2 \cdot 10^3$  Pa·sec on substrates consisting of single-crystal silicon, after calcination at  $700^\circ\text{C}$ . The results (Fig. 4) show that the film possesses a globular structure, consisting of 50 – 100 nm wide, 200 – 500 nm long, and 5 – 10 nm high blocks.

The main physical – chemical properties were studied for the thin-film system  $\text{SiO}_2 - \text{P}_2\text{O}_5$ . The change of the properties of the films as a function of the FFS composition is shown in Fig. 4. As the phosphorus oxide content in the films increases, their thickness decreases and the index of refraction increases. Films with 15 – 20%  $\text{P}_2\text{O}_5$  have the highest index of refraction, which could be due to structural rearrangements. For films with all compositions the permittivity is 2.4 – 2.6, the band gap is 5.8 – 6.2 eV, and the resistivity is  $10^{16} \Omega \cdot \text{cm}$ .

The films obtained are insulators and possess good adhesion to glass, single-crystal silicon, and quartz substrates.

In summary, the sol-gel method was used to obtain from FFS based on tetraethoxysiloxane and phosphoric acid, ethyl alcohol, and water thin films and disperse products in the system  $\text{SiO}_2 - \text{P}_2\text{O}_5$  with molar content of phosphorus oxide from 0 to 30%.

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